

Organic Aerosols in the Gulf of Maine: Perspective from the 2002 New England Air Quality Study



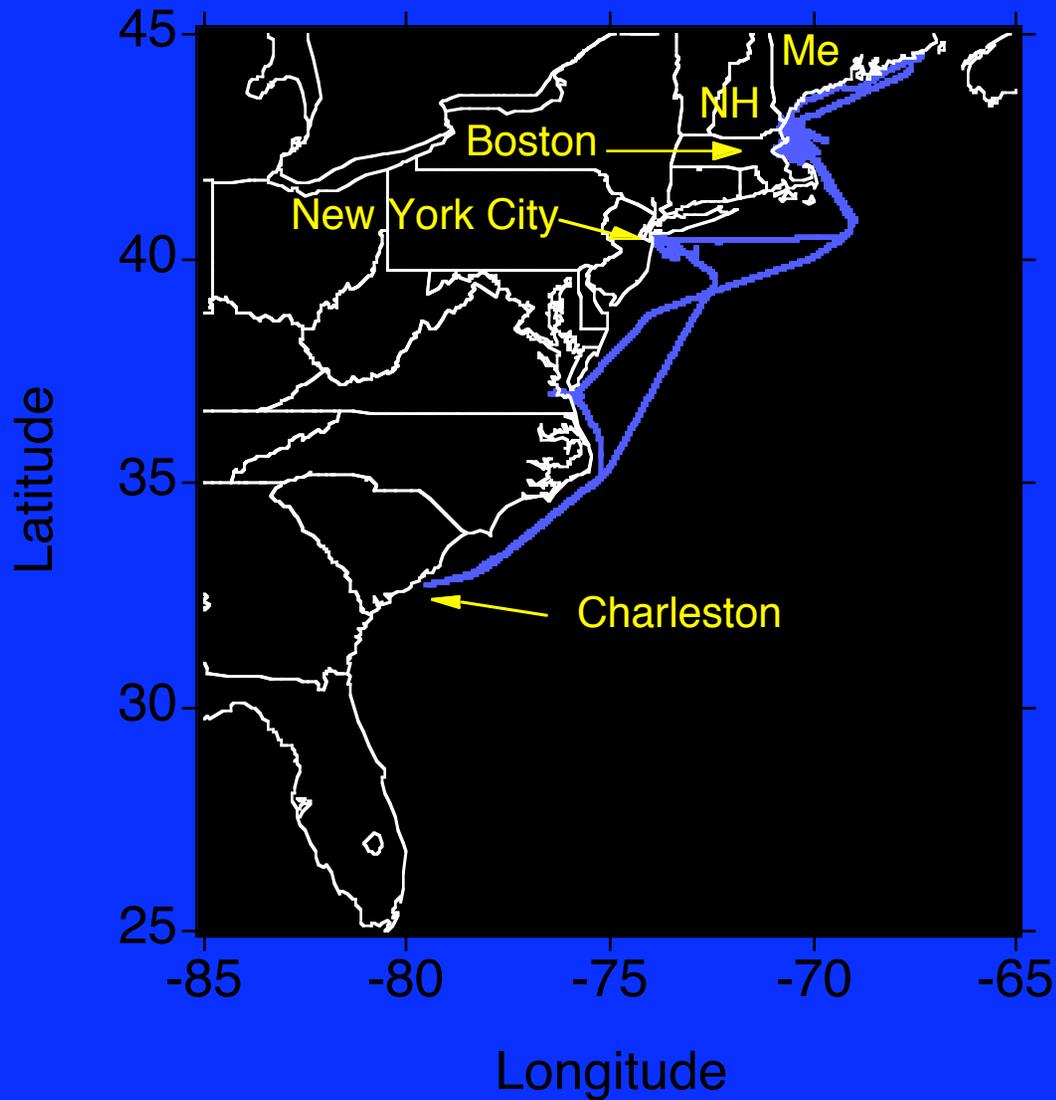
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1. Quantitative separation of different POM sources
primary and secondary, anthropogenic and biogenic
2. Organic carbon as a function of photochemical age
gas and particle phase

New England Air Quality Study (NEAQS) in 2002



Ship-based measurements off the U.S. East coast during July-August 2002



Measurements of Organic Carbon during NEAQS

Particle phase:

Sub- μm organic matter (POM)

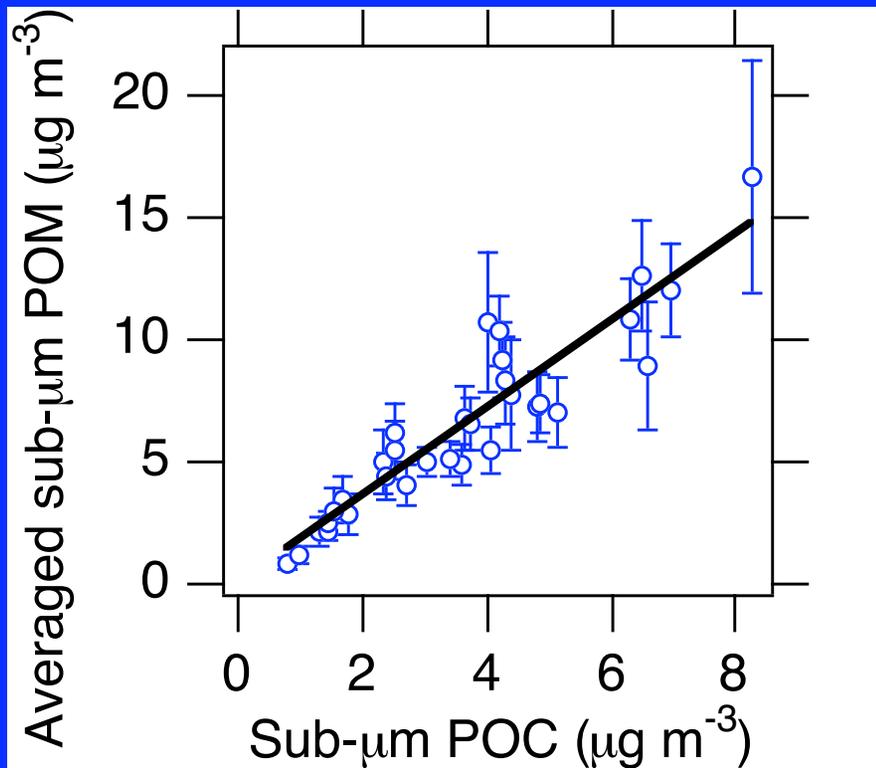
Sub- and super- μm organic carbon (POC)

AMS

impactors

Middlebrook

Bates



- POM and POC correlated: $r = 0.93$
- $\text{POM/POC} = 1.78 \pm 0.13$
- Super- $\mu\text{m} < 20\%$ of sub- μm POC

Measurements of Organic Carbon during NEAQS

Gas phase:

VOCs

PTR-MS

de Gouw

VOCs, alkyl nitrates

GC-MS

Goldan

PANs

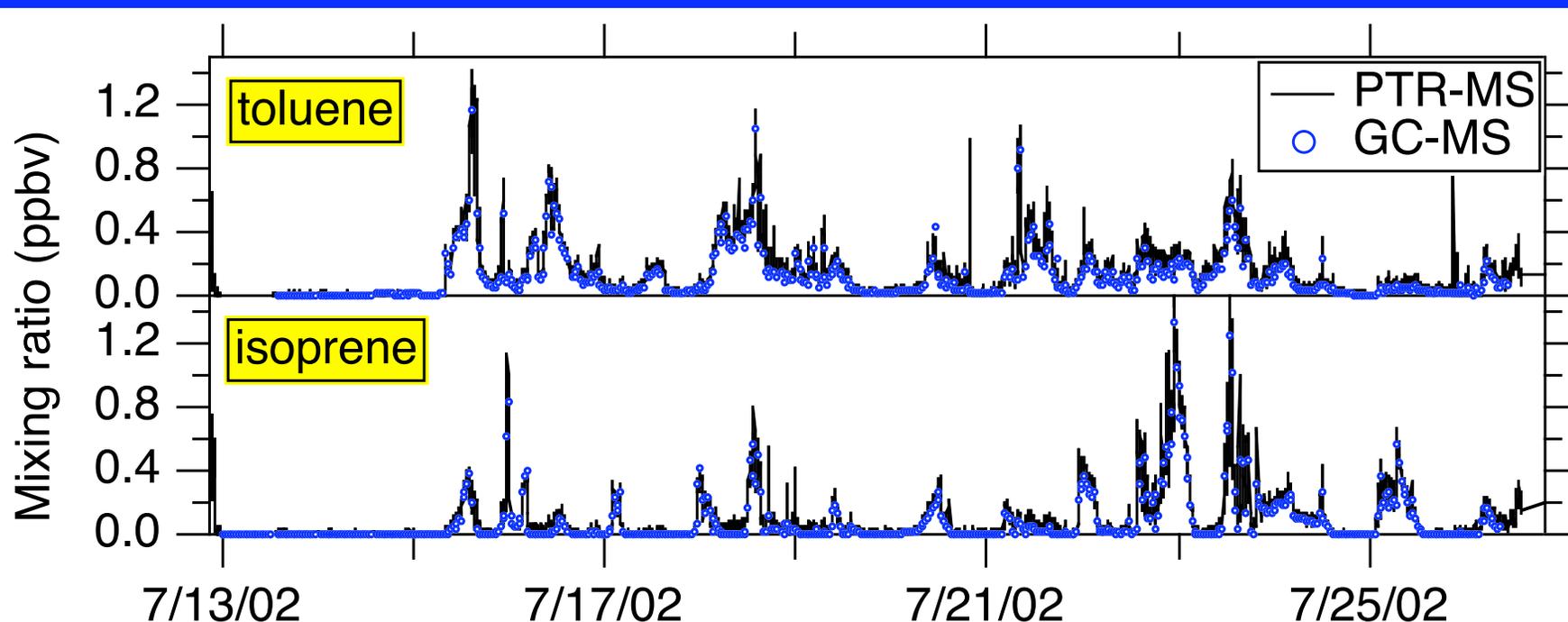
GC-ECD

Roberts

Organic acids

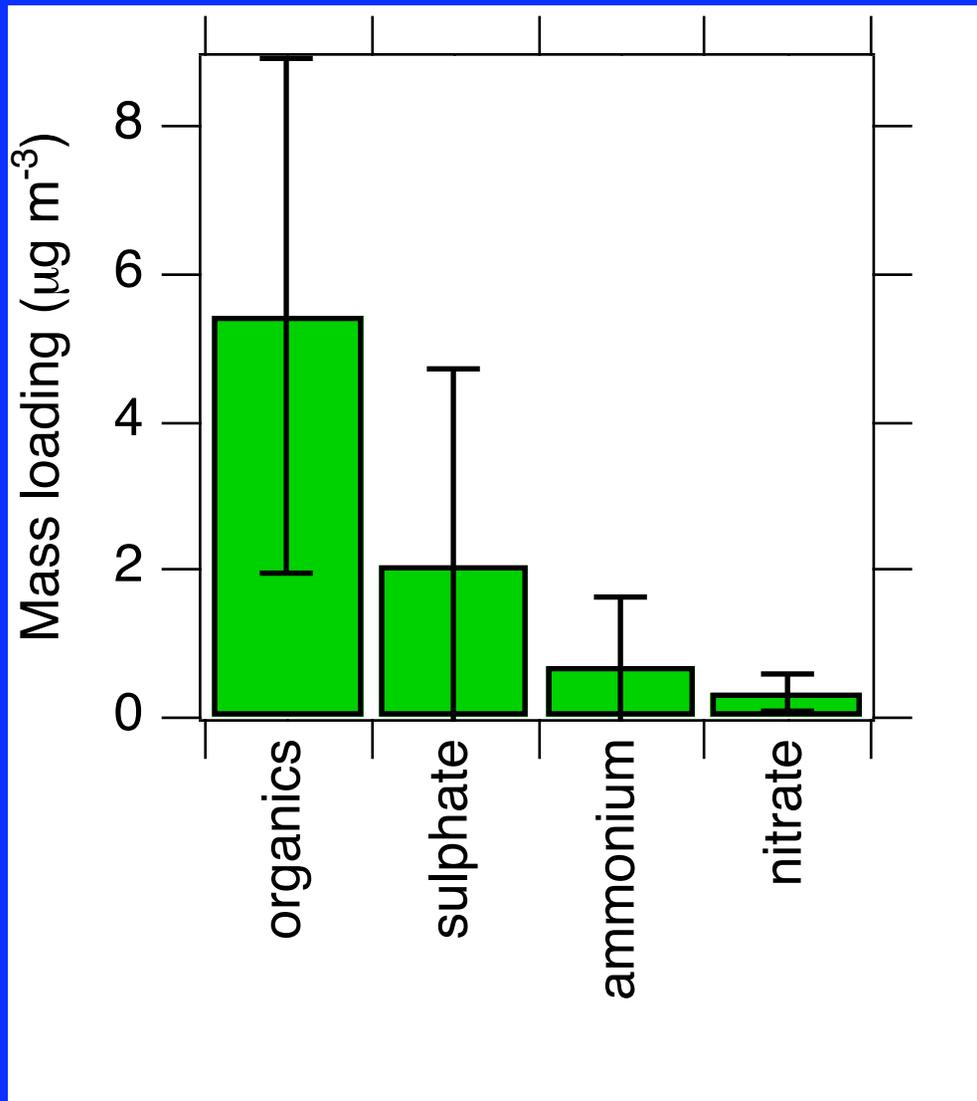
MC-IC

Keene, Pszenny



➤ Gas-phase measurements inter-compared [*de Gouw et al.*, JGR 2003]

Average Mass Loadings Measured by AMS

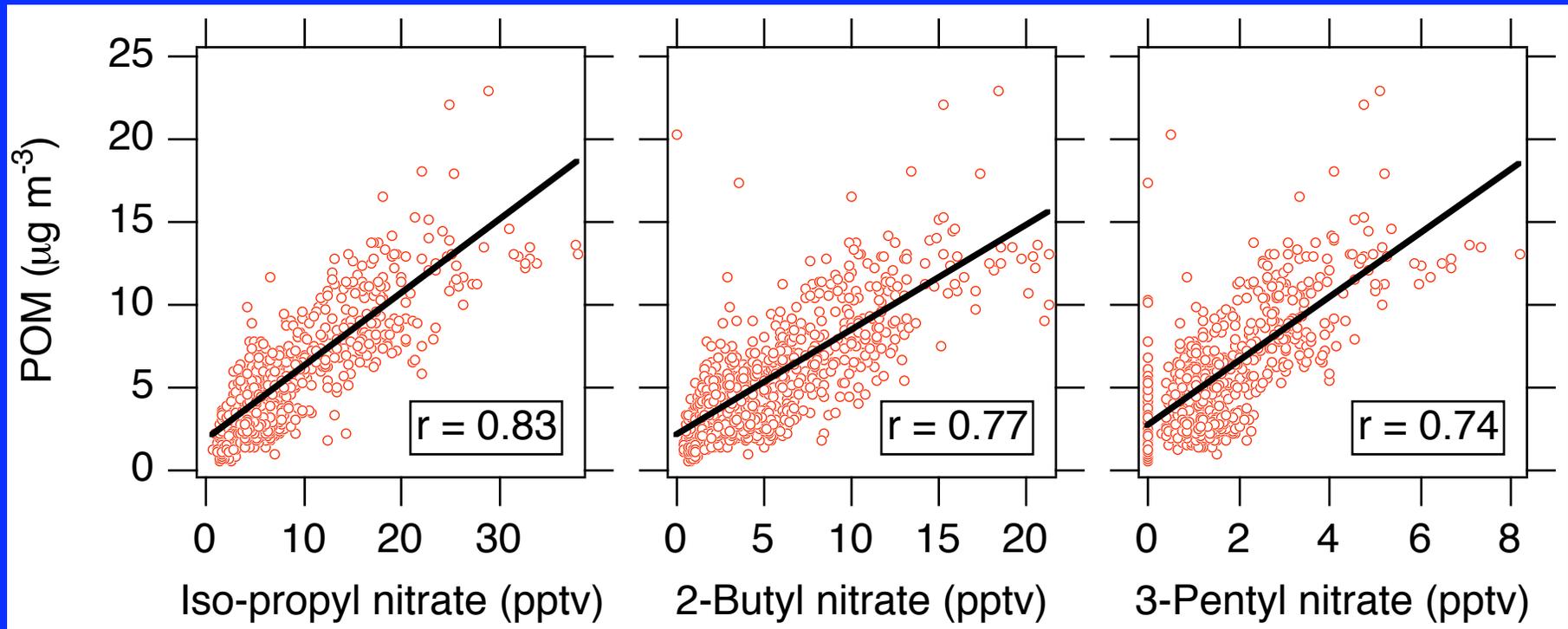


Particulate organic matter (POM) was the dominant sub- μm species.

also observed by *Quinn and Bates* [GRL 2003]

What are the sources of POM in New England?

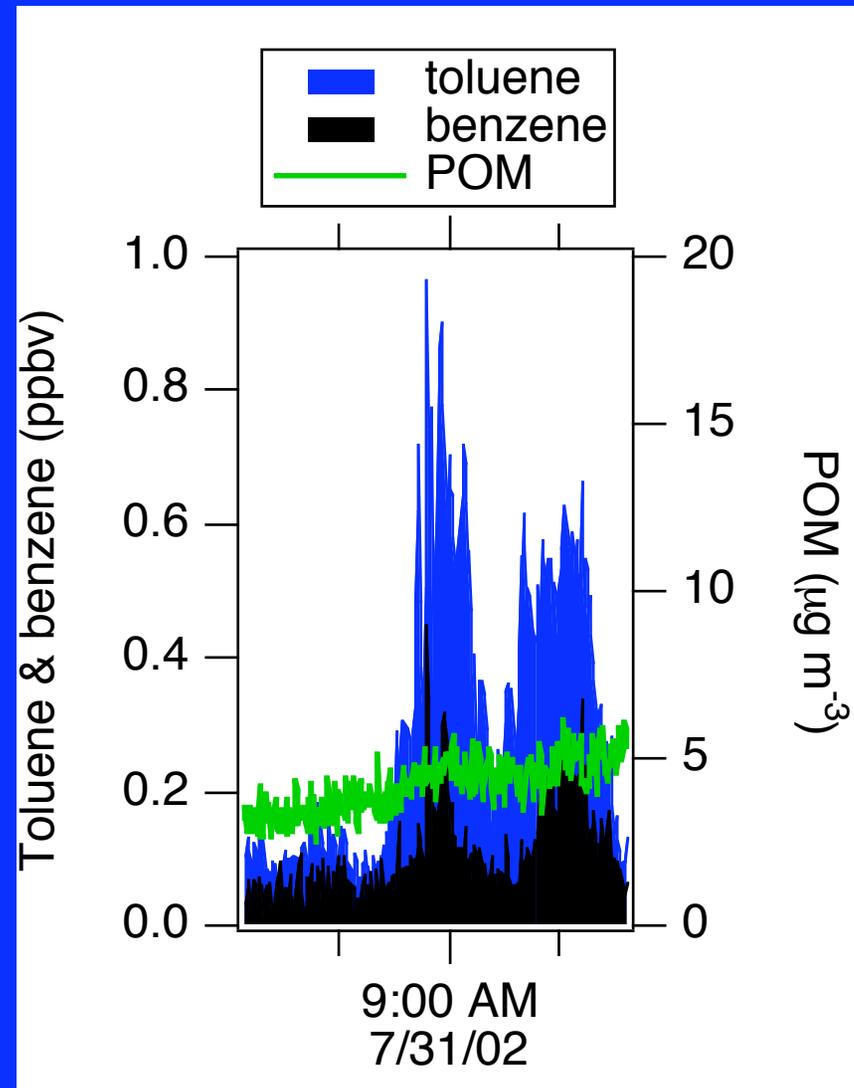
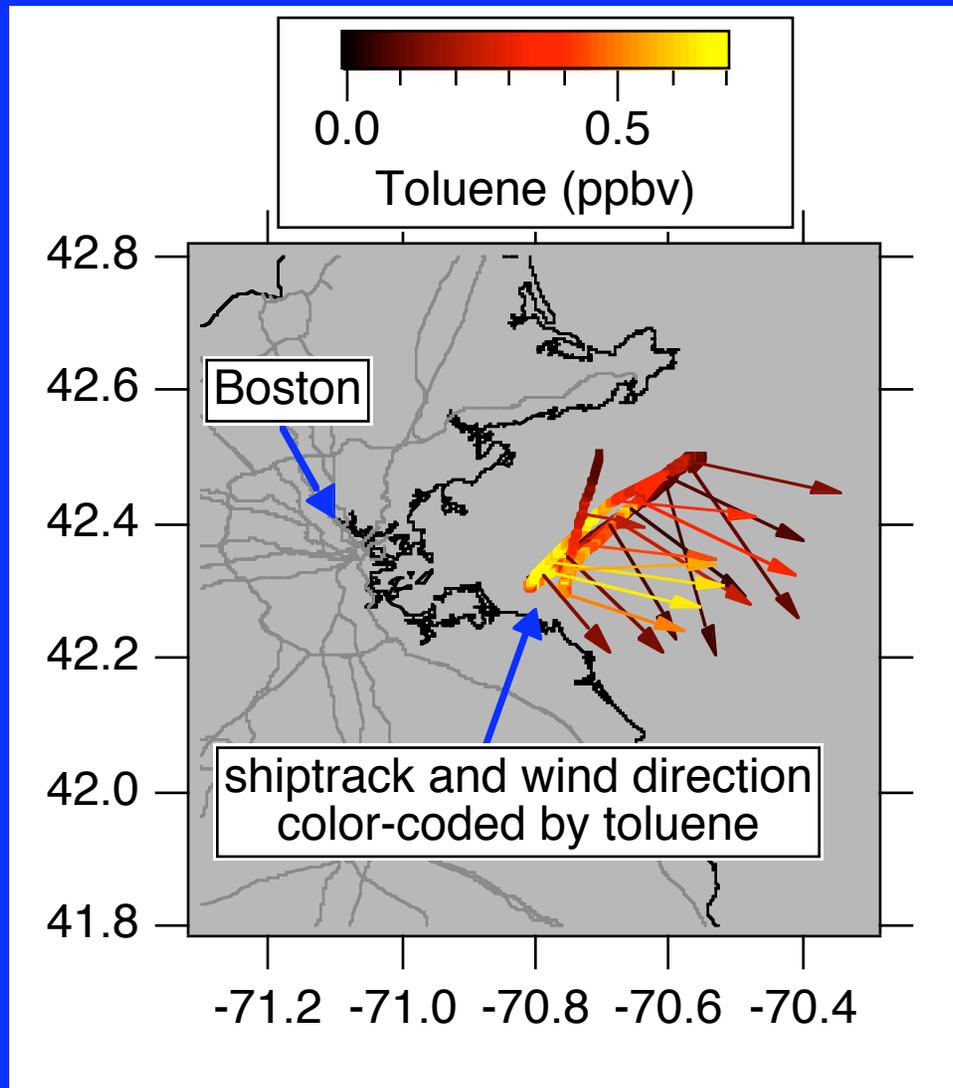
Correlation Between POM and Alkyl Nitrates



Suggests most of the POM was secondary from anthropogenic precursors

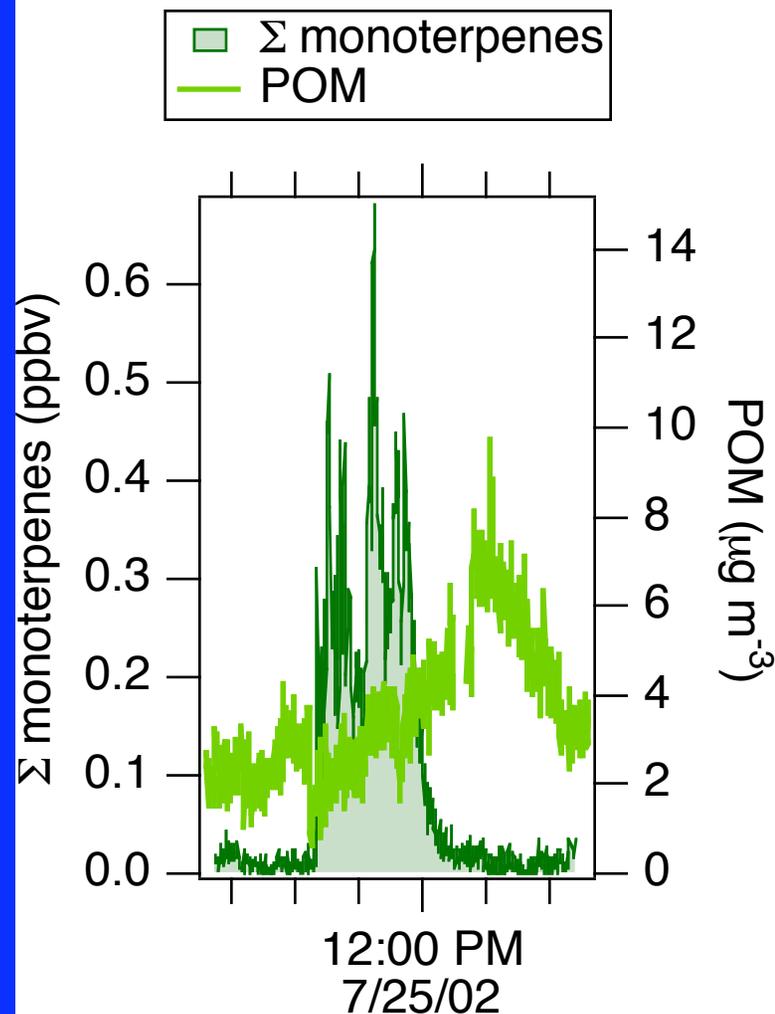
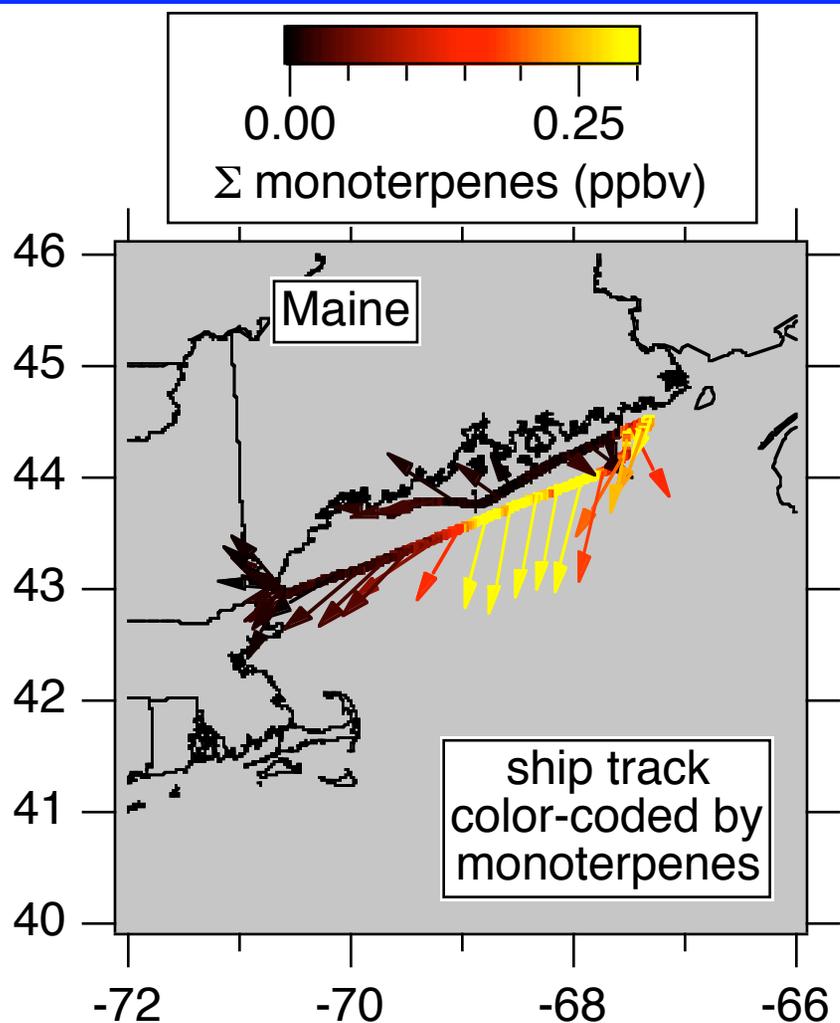
- What about primary emissions of POM ?
- What about biogenic precursors of POM ?

Primary Sources of POM



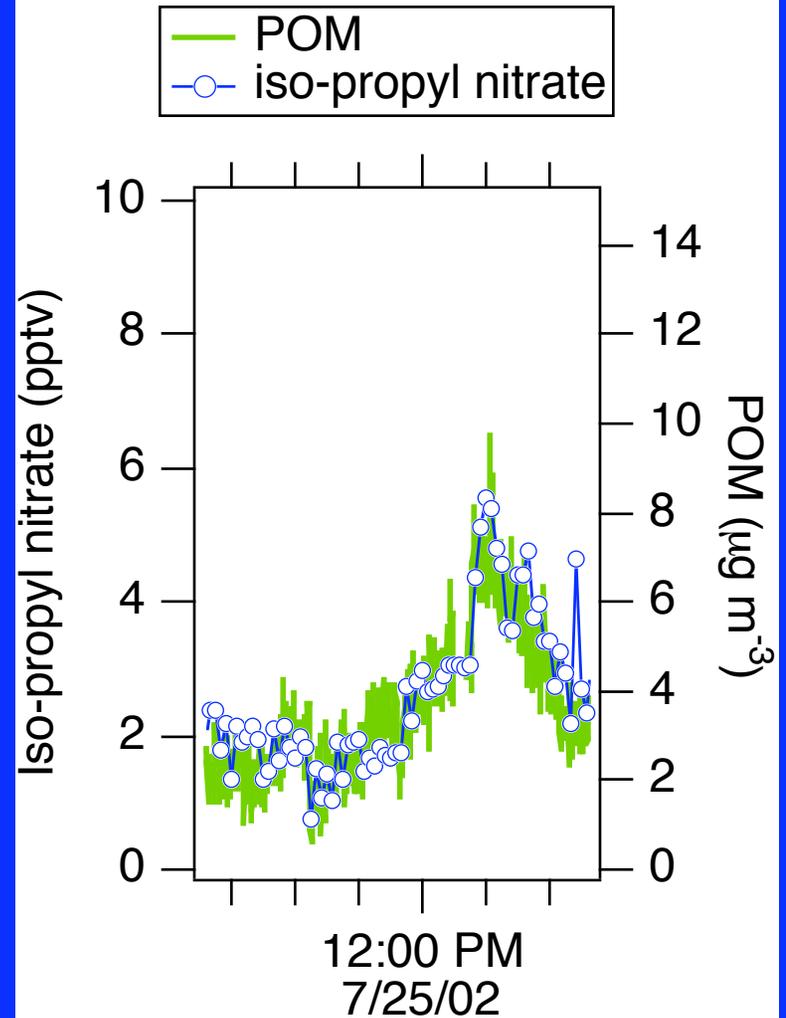
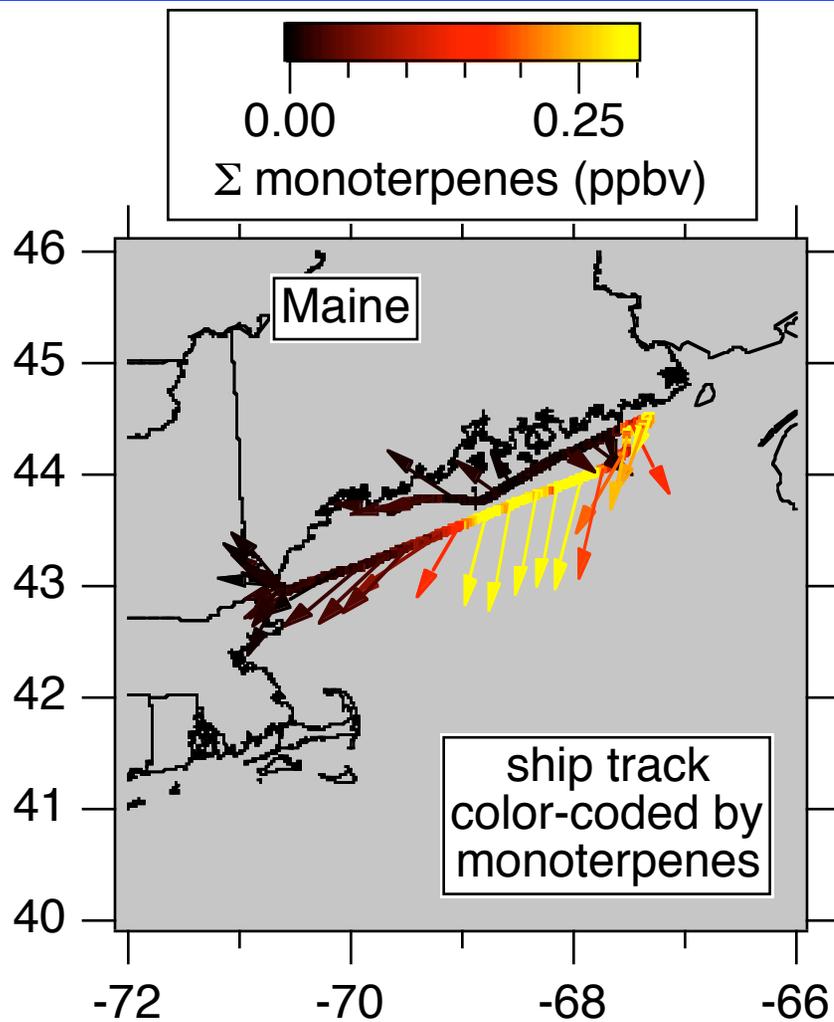
POM shows minor enhancements close to urban sources

Biogenic Sources of POM



Minor POM enhancements downwind of large biogenic sources

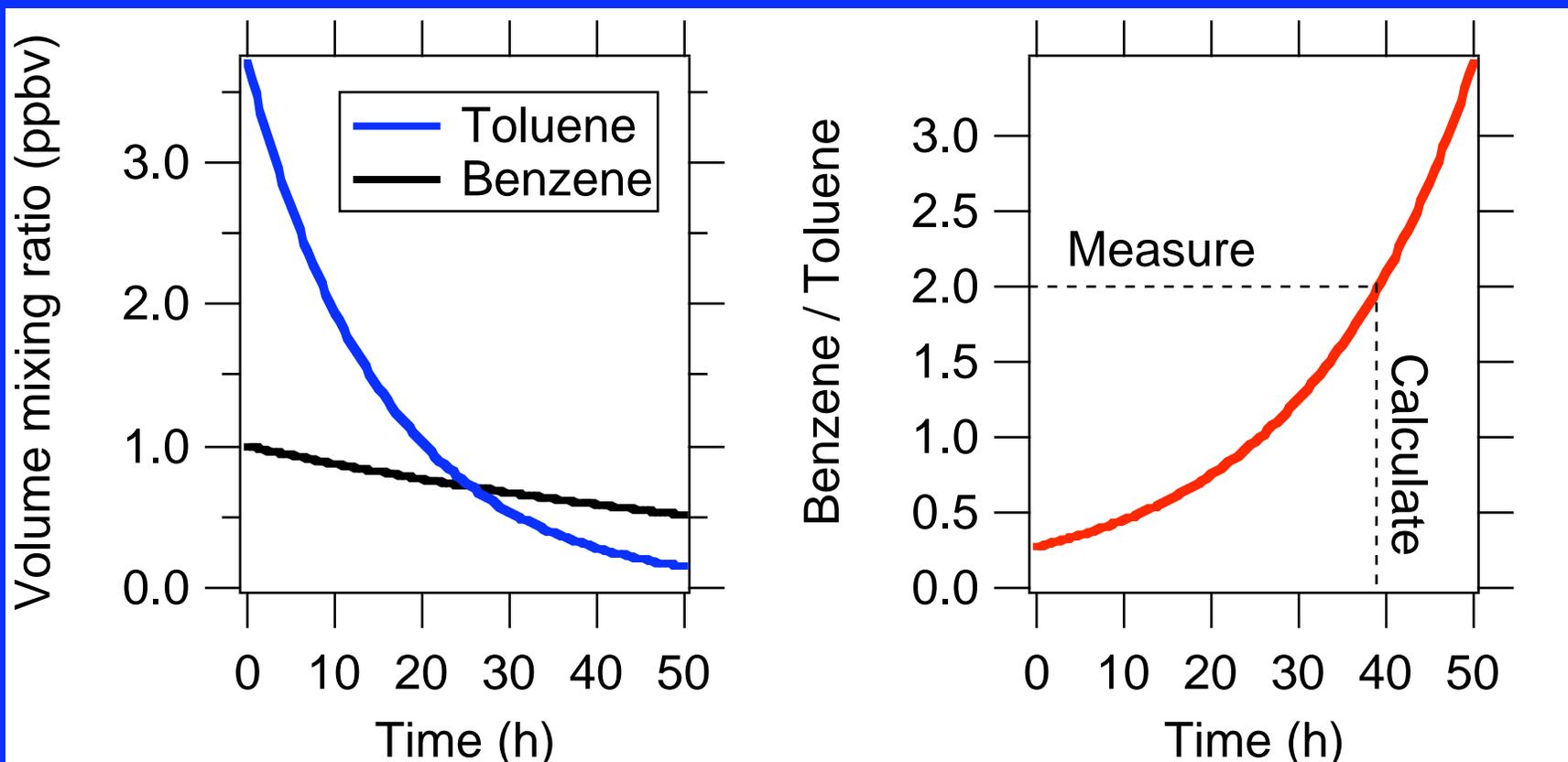
Biogenic Sources of POM



Minor POM enhancements downwind of large biogenic sources

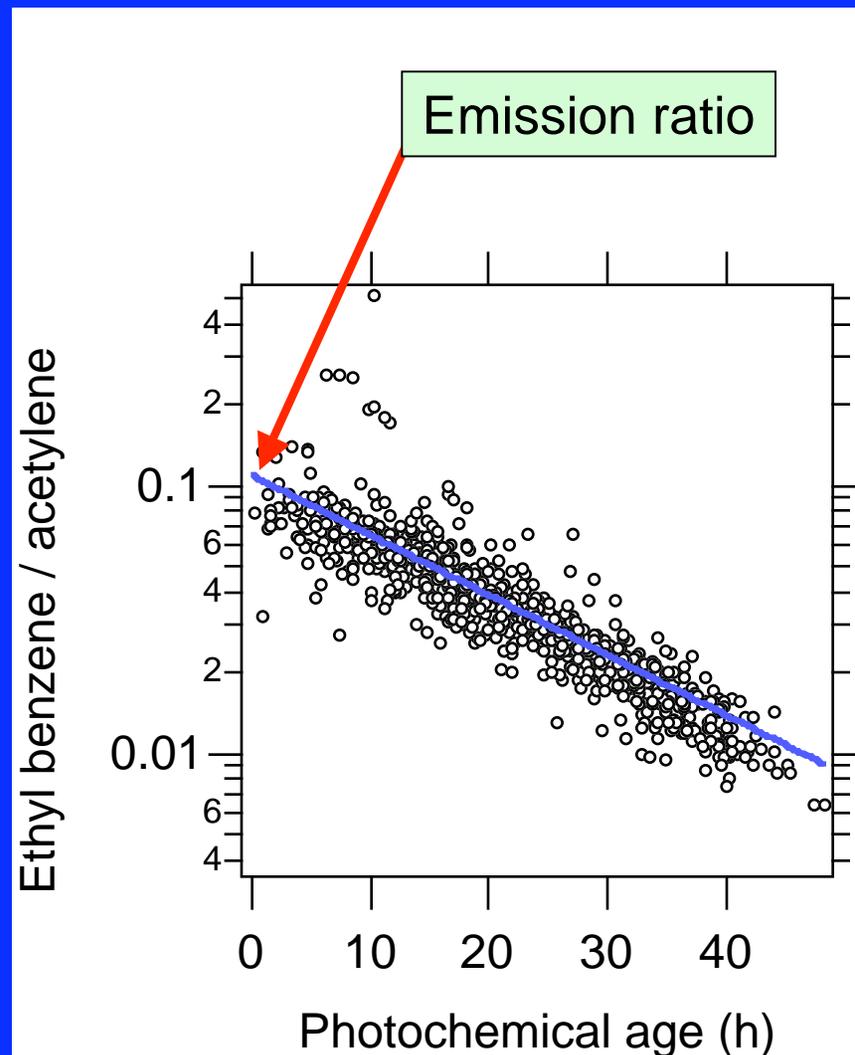
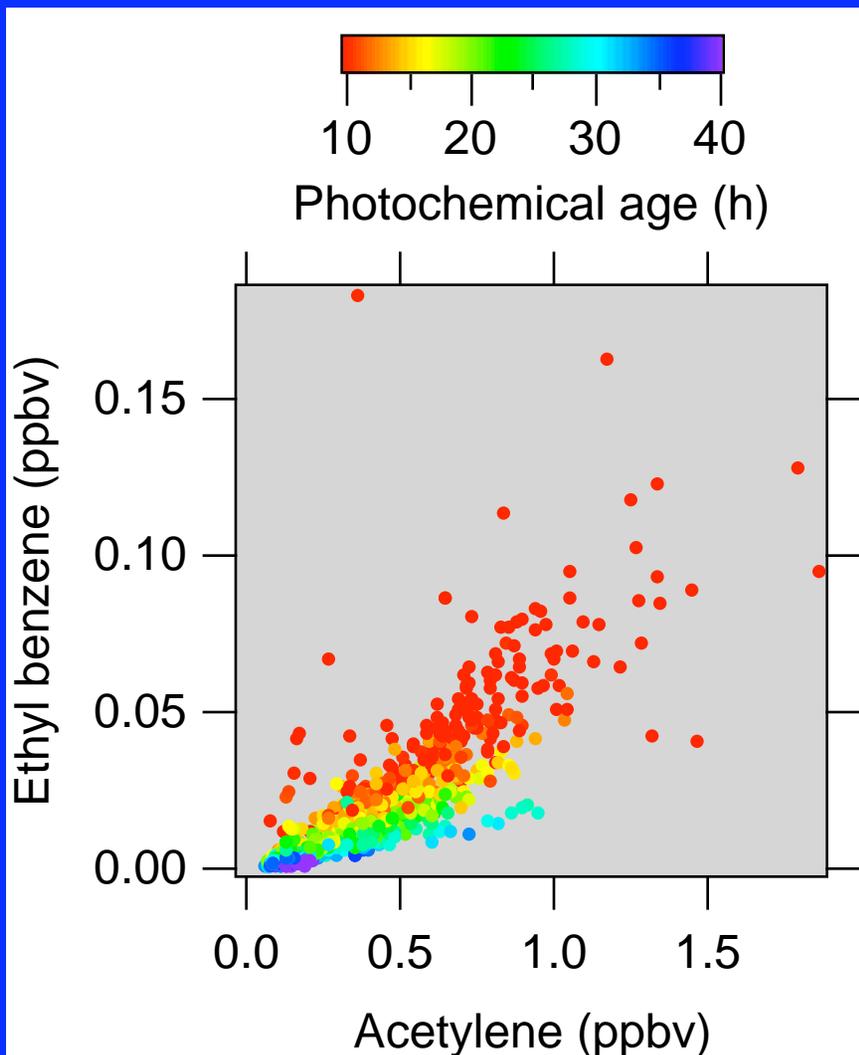
Determination of Photochemical Age

time since emission of the trace gases



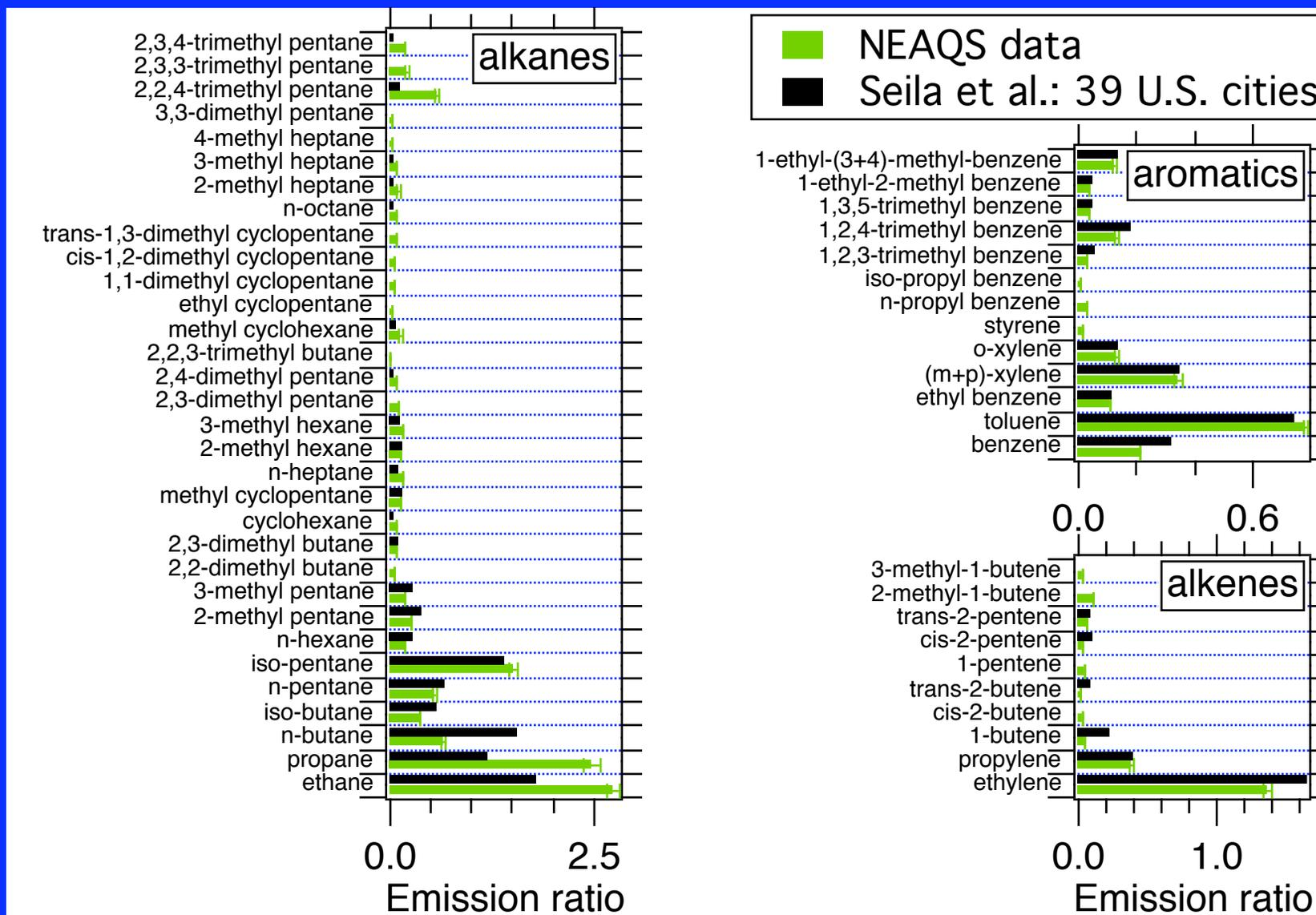
- Benzene and toluene are emitted from vehicles at a constant ratio
- Toluene is 4.8× faster removed than benzene

Primary Anthropogenic VOCs versus Photochemical Age



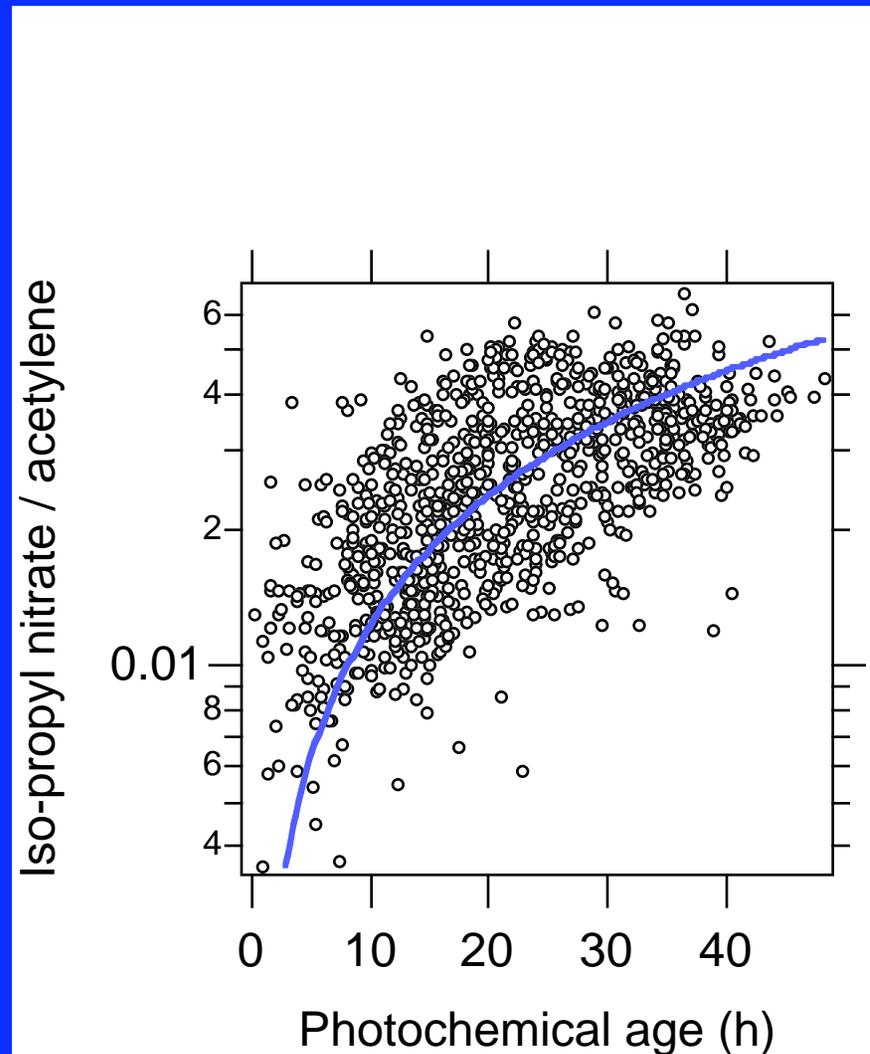
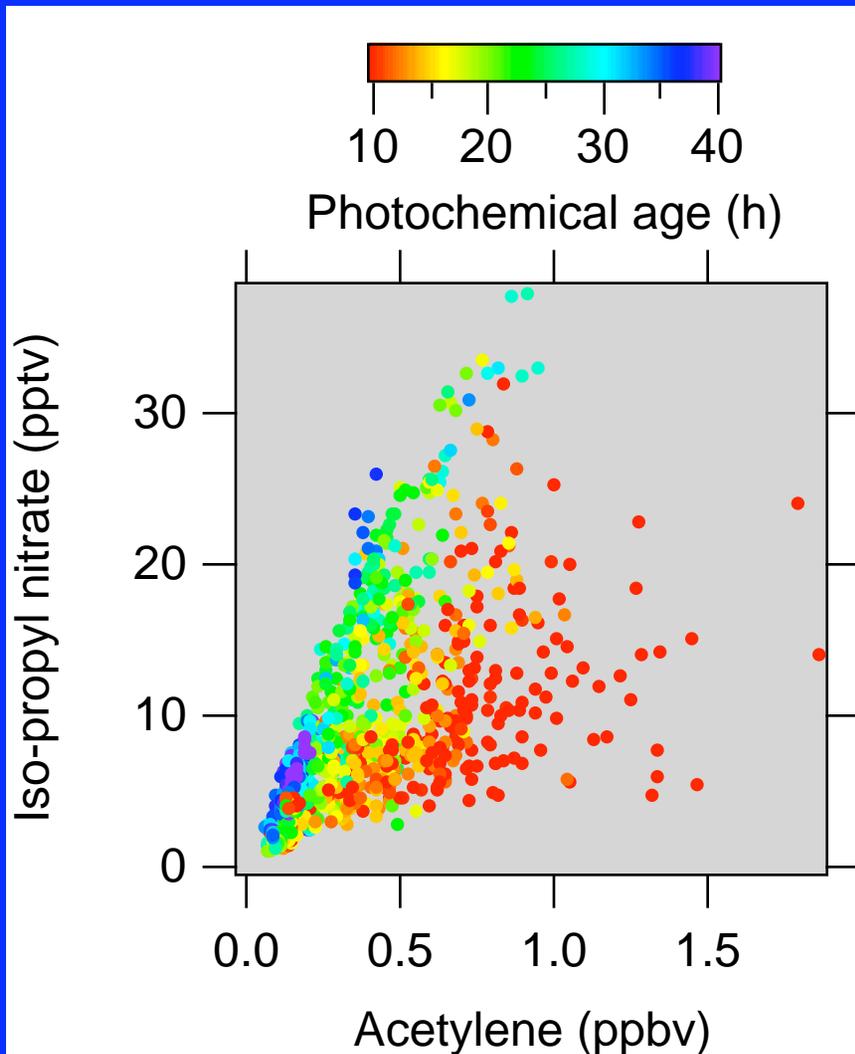
Ethyl benzene is more reactive than acetylene \Rightarrow ratio decreases with age

Comparison of Emission Ratios



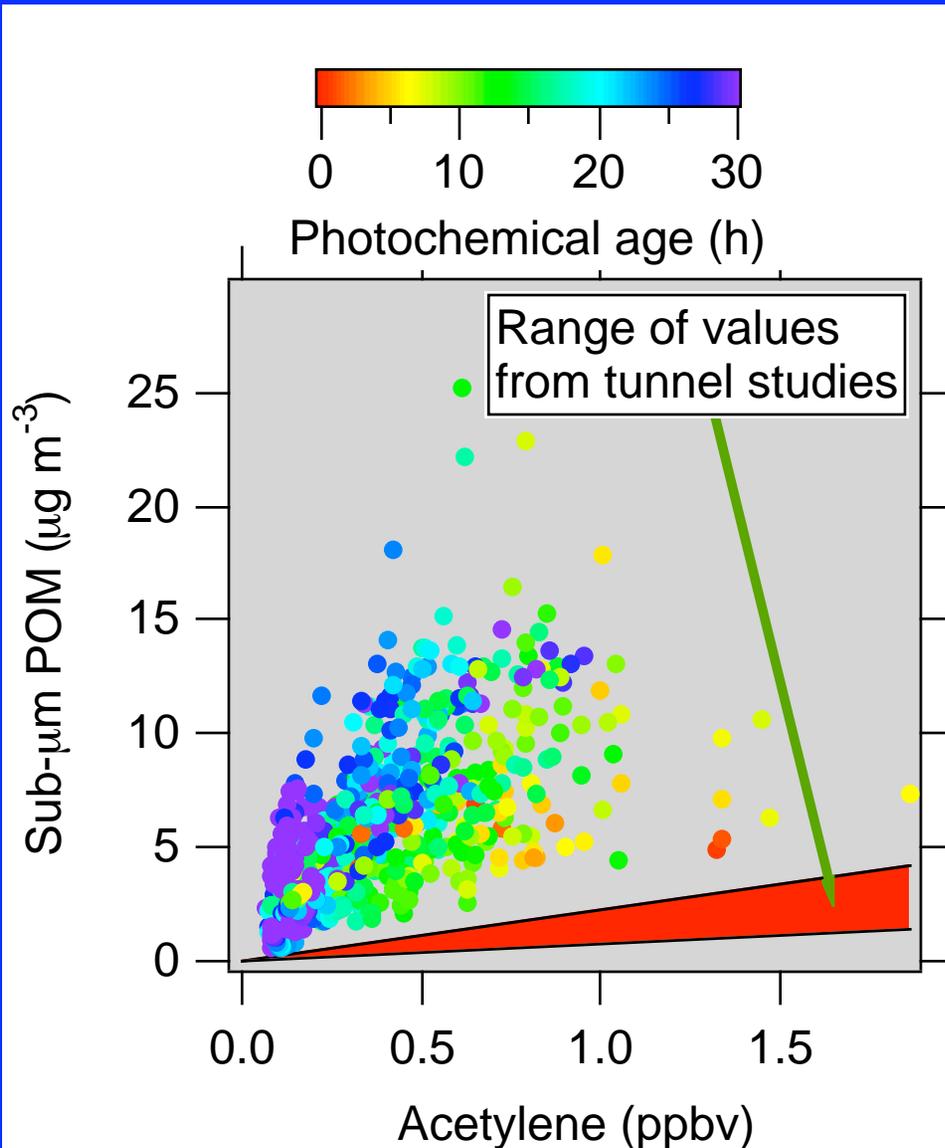
At zero age: VOC composition equals that of average U.S. city

Iso-Propyl Nitrate versus Photochemical Age



Fit: Propane assumed to be precursor
Yield (only free parameter) 3.7%
Literature value 2.9%

POM versus Photochemical Age



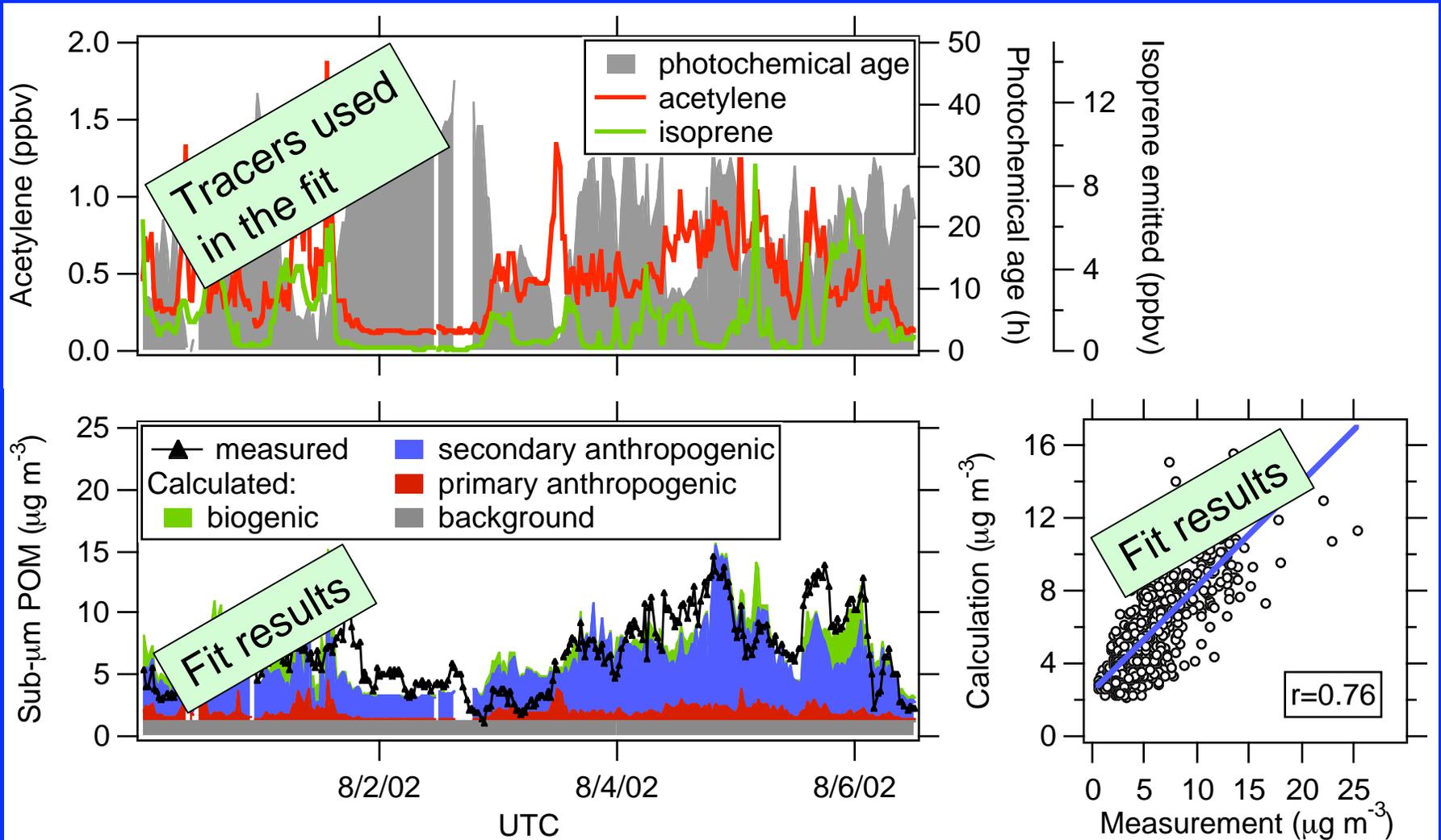
- Enhancement of POM versus acetylene increases as the air mass is processed
- Importance of secondary POM formation

Quantitative Separation of VOC and POM Sources

Basic assumptions:

1. Primary anthropogenic emissions of VOCs and POM are proportional to those of acetylene
2. Removal of primary anthropogenic VOCs and POM, and formation of secondary anthropogenic species is governed (i) by the photochemical age and, as much as possible, (ii) by the reaction kinetics
3. Primary and secondary biogenic contributions of VOCs and POM are proportional to the emissions of isoprene

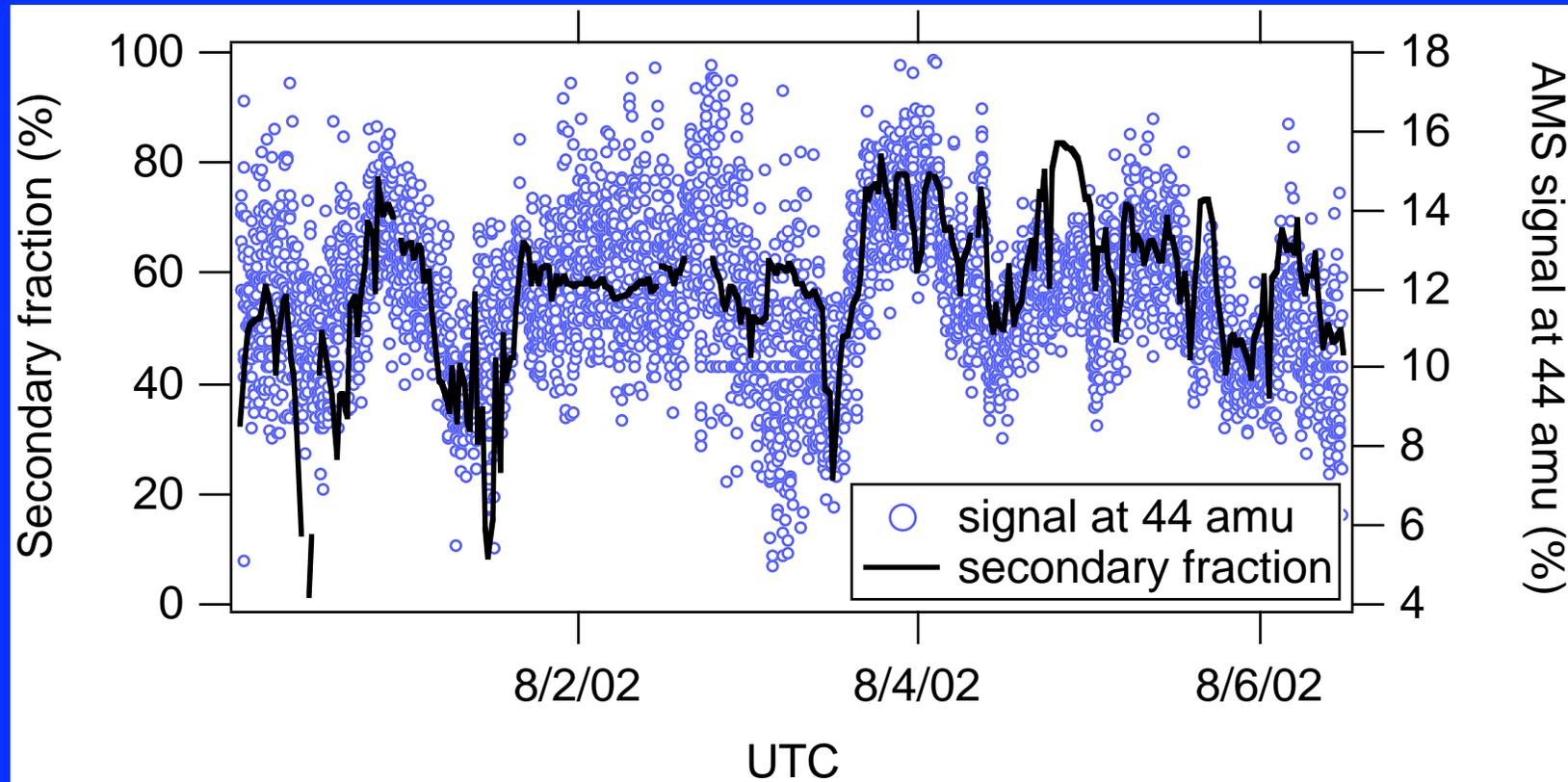
Separation of the POM Sources



Primary anthropogenic 6%
 Secondary anthropogenic 66%

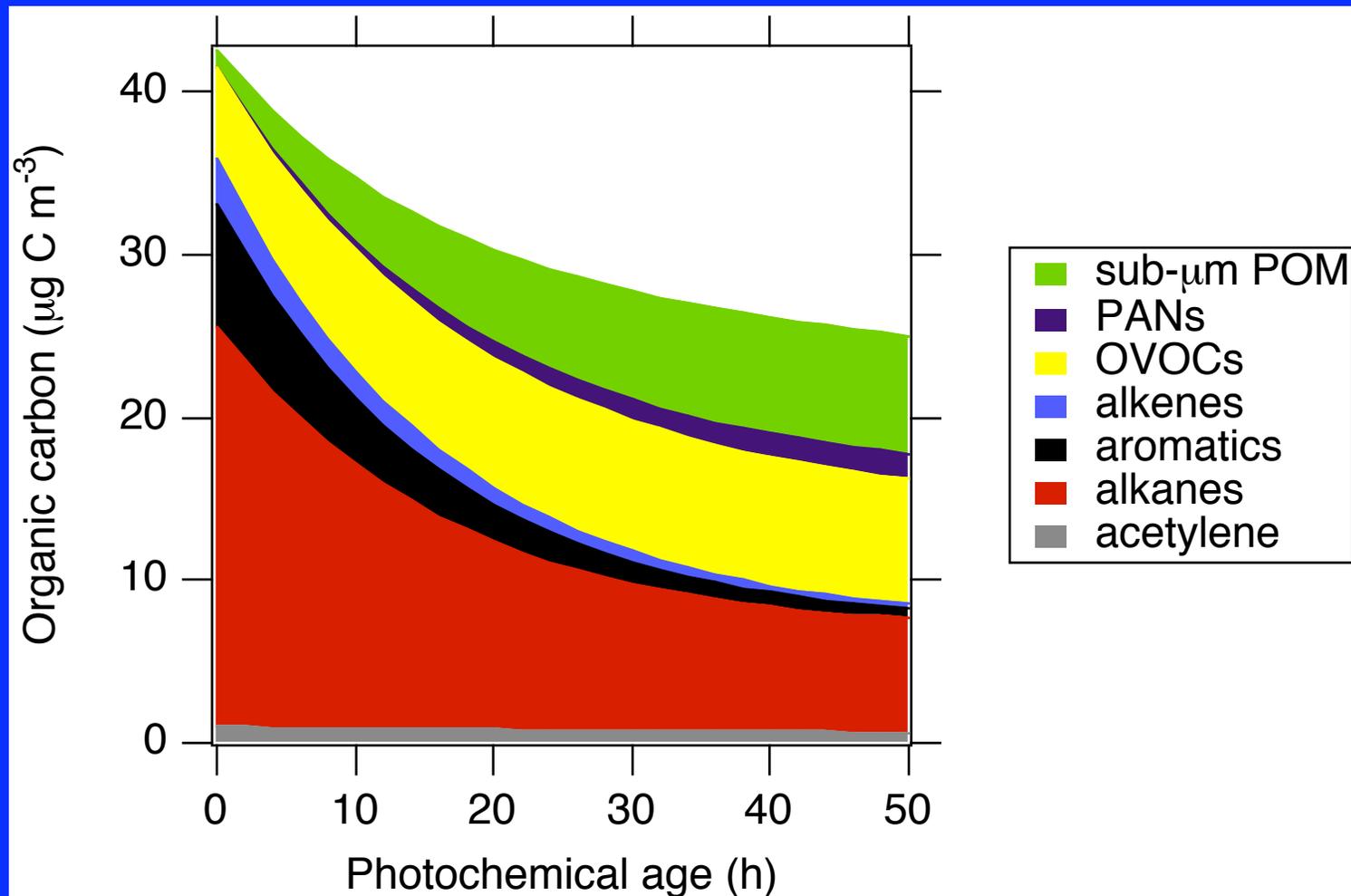
Biogenic 6%
 Background 22%

Secondary Fraction from Multivariate Fit vs. AMS Signal at 44 amu



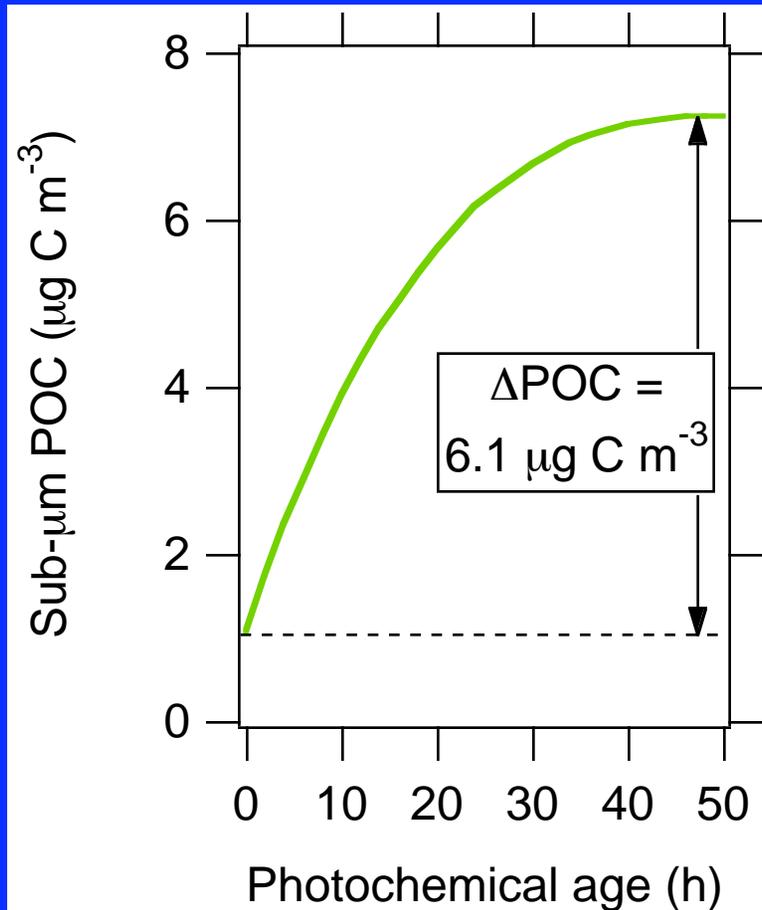
The higher the secondary fraction of the POM, the more processed the particles were according to the AMS

Anthropogenic Organic Carbon versus Photochemical Age



- POM, OVOCs and PANs increase with age; the rest decreases
- Total organic carbon approximately conserved
- Decrease of ~40% due to deposition?

Formation of Secondary Anthropogenic POM



$$\text{Secondary POC yield} = \sum_{i=1}^{32} [\text{alkanes}]_i Y_i + \sum_{j=1}^{13} [\text{aromatics}]_j Y_j + \sum_{k=1}^{10} [\text{alkenes}]_k Y_k$$

where Y_i is the potential yield for species i [Seinfeld and Pandis].

alkanes	0.09
aromatics	0.34
<u>alkenes</u>	<u>0.00</u>
total	0.43 $\mu\text{g C m}^{-3} (\text{ppbv C}_2\text{H}_2)^{-1}$

Less than 10% of secondary formation of POC can be attributed to known precursors!

What does it mean?

1. Are other precursors more important?
 - *80% of species in vehicle exhaust was measured*
 - *Paulson et al.: 85% of TOC can be identified by GC*
2. Formation of secondary POM continues longer than accounted for by smog-chamber experiments?
3. Is the biogenic contribution properly accounted for?
 - *Radiocarbon dating of POM typically gives higher modern fraction*
 - *POM formation from biogenic precursors may be more efficient in polluted conditions*

Conclusions

- POM in New England region was mostly attributed to secondary anthropogenic sources
- The primary and biogenic fractions of POM were surprisingly small
- The total mass of organic carbon decreased by ~40% in the first 2 days after emission
- The increase in POC could not be explained by the decrease in known precursors

Acknowledgements

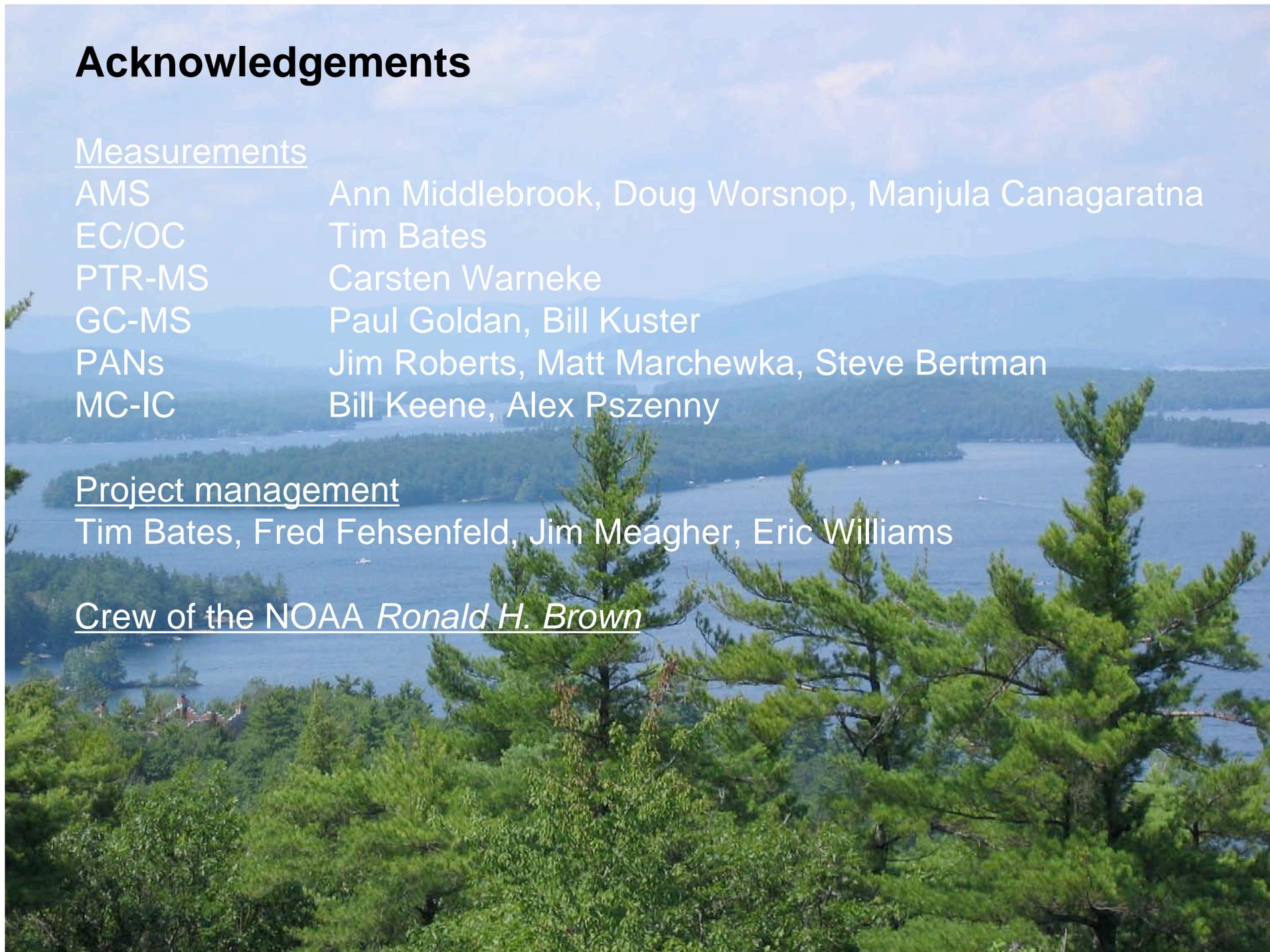
Measurements

AMS	Ann Middlebrook, Doug Worsnop, Manjula Canagaratna
EC/OC	Tim Bates
PTR-MS	Carsten Warneke
GC-MS	Paul Goldan, Bill Kuster
PANs	Jim Roberts, Matt Marchewka, Steve Bertman
MC-IC	Bill Keene, Alex Pszenny

Project management

Tim Bates, Fred Fehsenfeld, Jim Meagher, Eric Williams

Crew of the NOAA *Ronald H. Brown*



Can we separate Secondary Anthropogenic and Secondary Biogenic Sources?

Perform same analysis for PANs:

Williams et al. 1998:

PPN	secondary anthropogenic
MPAN	secondary biogenic
PAN	both

This analysis:	Primary Anthropogenic	Secondary Anthropogenic	Biogenic
PPN	0%	97%	3%
MPAN	0%	14%	86%
PAN	0%	75%	25%

Analysis of PANs confirms that secondary anthropogenic and secondary biogenic sources are mostly separated by the method